IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of Nobuyuki IWASAKI et al.

Appln. No. 09/988,466 Group Art Unit: 1774

Filed: November 20, 2001 Examiner: B. H. Hess

For: HEAT-SENSITIVE RECORDING MATERIALS

DECLARATION

Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Nobuyuki IWASAKI, researcher, Imaging Media Development Laboratory, Oji Paper Co., Ltd., hereby declare that:

1) I am one of the inventors of the instant invention;

2) I graduated from Kyushu Institute of Technology in 1990 and joined Honshu Paper Co., Ltd. in 1990, and since then I have been doing research on general papers, especially research on heat-sensitive recording materials for 12 years, and have continued in this research up to now (Honshu Paper Co., Ltd. became Oji Paper Co., Ltd. through a merger with New Oji Paper Co., Ltd. in August 1996); and

3) the experiments given below were carried out by myself.

I. PURPOSE

To show the significance of using specific inorganic pigment(s) (at least one selected from aluminum hydroxide, amorphous silica, kaolin, and talc) in the specific amount (3 to 50 wt% based on the heat-sensitive recording layer) defined in claim 1 of the present invention.

II. EXPERIMENTS

Experiment 1

Preparation of undercoat layer coating composition

A composition composed of 60 parts of calcined clay (trade name: Ansilex, oil absorption 110 ml/100 g, made by Engelhard Corporation), 100 parts of a 20% dispersion of organic expandable hollow particles (inside diameter/outside diameter = 0.95: shell material = polyvinylidene chloride) which expand to an average particle diameter of about 5 μm upon expansion, 1 part of a 40% aqueous solution of a polyacrylic acid sodium salt, 14 parts of a styrene-butadiene latex with a solids concentration of 48%, 50 parts of a 10% aqueous solution of polyvinyl alcohol (degree of saponification: 88%, degree of polymerization: 1000) and 40 parts of water was mixed and stirred to obtain an undercoat layer coating composition.

Preparation of Dispersion A

A composition composed of 10 parts of N-p-toluene-sulfonyl-N'-3- (p-toluenesulfonyloxy)phenylurea, 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water

was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion A.

Preparation of Dispersion B

A composition composed of 10 parts of a fluoran-based leuco dye which forms black color, i.e., 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point : 206°C), 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion B.

Preparation of Dispersion C

A composition composed of 10 parts of 1,2-di(3-methylphenoxy)ethane, 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion C.

Preparation of Dispersion D

A composition composed of 40 parts of aluminum hydroxide (trade name: Higilite H42, made by Showa Denko, average particle diameter of primary particles: 1 μm), 1 part of a 40% aqueous solution of a polyacrylic acid sodium salt and 40 parts of water was mixed and stirred to obtain Dispersion D.

Preparation of heat-sensitive recording layer coating composition

120 parts of Dispersion A, 40 parts of Dispersion B, 80 parts of Dispersion C, 40 parts of Dispersion D, 160 parts of

a 10% aqueous solution of polyvinyl alcohol (degree of polymerization: 100, degree of saponification: 98%), 20 parts of a styrene-butadiene latex with a solids concentration of 50% and 12.5 parts of a 40% aqueous solution of glyoxal were mixed and stirred to obtain a heat-sensitive recording layer coating composition.

Preparation of protective layer coating composition

500 parts of a 10% aqueous solution of acetoacetyl-modified polyvinyl alcohol (trade name: Gohsefimer Z200, made by The Nippon Synthetic Chemical Industry Co., Ltd.), 40 parts of a 50% aqueous; dispersion of kaolin (trade name UW-90, made by Engelhard Corporation) and 40 parts of a 50% aqueous dispersion of aluminum hydroxide (trade name: Higilite H42, made by Showa Denko) were mixed and stirred to obtain a protective layer coating composition.

Production of heat-sensitive recording material

One side of wood free paper (neutral paper) weighing 64 g/m^2 was coated with the above undercoat layer coating composition such that the coating amount was 7 g/m^2 on dry weight basis, and the coating was dried. This coated side was then brought into close contact with a chromium-plated, mirror-finish metal hot roll (120°C). This heat-treatment caused the organic expandable particles to expand, whereby an undercoat layer was formed.

The undercoat layer thus formed was coated with the

heat-sensitive recording layer coating composition such that the coating amount after drying was 6 g/m^2, and the coating was dried to form a heat-sensitive recording layer.

The resulting heat-sensitive recording layer was then coated with the protective layer coating composition such that the coating amount after drying was 3 g/m^2 to obtain a heat-sensitive recording material. The heat-sensitive recording material thus obtained was subjected to a surface smoothing treatment with a super calender.

Experiment 1 was conducted in the same manner as in Example 1 in the present specification.

Experiment 2

A heat-sensitive recording material was obtained in the same manner as in Experiment 1 except that 150 parts of Dispersion A, 50 parts of Dispersion B, 100 parts of Dispersion C, 12 parts of Dispersion D was used in Experiment 1.

Experiment 3

A heat-sensitive recording material was obtained in the same manner as in Experiment 1 except that 60 parts of Dispersion A, 20 parts of Dispersion B, 40 parts of Dispersion C, 100 parts of Dispersion D was used in Experiment 1.

Experiment 4

A heat-sensitive recording material was obtained in the same manner as in Experiment 2 except that amorphous silica (trade name Mizukasil P-603, made by MIZUSAWA INDUSTRIAL

CHEMICALS,LTD.) was used in place of aluminum hydroxide in the preparation of Dispersion D in Experiment 2.

Experiment 5

A heat-sensitive recording material was obtained in the same manner as in Experiment 3 except that amorphous silica (trade name Mizukasil P-603, made by MIZUSAWA INDUSTRIAL CHEMICALS,LTD.) was used in place of aluminum hydroxide in the preparation of Dispersion D in Experiment 3.

Experiment 6

A heat-sensitive recording material was obtained in the same manner as in Experiment 2 except that kaolin (trade name UW-90, made by Engelhard Corporation, average particle diameter of primary particles: 1 μm) was used in place of aluminum hydroxide in the preparation of Dispersion D in Experiment 2.

Experiment 7

A heat-sensitive recording material was obtained in the same manner as in Experiment 3 except that kaolin(trade name UW-90, made by Engelhard Corporation, average particle diameter of primary particles: 1 μm) was used in place of aluminum hydroxide in the preparation of Dispersion D in Experiment 3.

Experiment 8

A heat-sensitive recording material was obtained in the same manner as in Experiment 2 except that talc (trade name Hymicron, made by Takehara Kagaku Kabushiki Kaisha, average particle diameter of primary particles: 5 μm) was used in place

of aluminum hydroxide in the preparation of Dispersion D in Experiment 2.

Experiment 9

A heat-sensitive recording material was obtained in the same manner as in Experiment 3 except that talc (trade name Hymicron, made by Takehara Kagaku Kabushiki Kaisha, average particle diameter of primary particles: 5 μm) was used in place of aluminum hydroxide in the preparation of Dispersion D in Experiment 3.

Comparative Experiment 1

A heat-sensitive recording material was obtained in the same manner as in Experiment 1 except that 156 parts of Dispersion A, 52 parts of Dispersion B, 104 parts of Dispersion C, 4 parts of Dispersion D was used in Experiment 1.

Comparative Experiment 2

A heat-sensitive recording material was obtained in the same manner as in Experiment 1 except that 36 parts of Dispersion A, 12 parts of Dispersion B, 24 parts of Dispersion C, 130 parts of Dispersion D was used in Experiment 1.

Comparative Example 1

The data of heat-sensitive recording material in Comparative Example 1 were taken from Table 1 of the present specification.

III. EVALUATION OF RECORDING PROPERTIES

The heat-sensitive recording materials obtained above were subjected to the following evaluation tests, and the results are shown in Table 1.

Recording density

Using a thermosensitive printing tester (product name: TH-PMD, manufactured by Okura Denki Kabushiki Kaisha), each heat-sensitive recording material was colored at an applied energy of 0.50 mJ/dot, and the color density of the recorded image thus obtained was measured in visual mode with a Macbeth densitometer (trade name: model RD-914, made by Macbeth).

Heat resistance

After recording in the measurement of recording density, the heat-sensitive recording material was left to stand for 5 hours in a dryer maintained at 90°C, and then the optical density of the unrecorded portion was measured with a Macbeth densitometer to evaluate the heat resistance.

Light resistance.

After recording in the measurement of recording density, the heat-sensitive recording material was left to stand for 24 hours in a xenon weatherometer (68 W/m^2 - 300 to 400 nm) maintained at 63°C ,and 40% RH, and then the optical density of the unrecorded portion and the optical density of the recorded image were measured with a Macbeth densitometer to evaluate the light resistance.

Water resistance

After recording in the evaluation of recording density, the heat-sensitive recording material was immersed for 24 hours in water at 20°C, and then the heat-sensitive recording material was allowed to dry naturally.

The optical density of the recorded image was measured with a Macbeth densitometer to evaluate the water resistance.

Hot water resistance

After recording in the evaluation of recording density, the heat-sensitive recording material was immersed for 30 seconds in hot water at 90°C, and then the heat-sensitive recording material was allowed to dry naturally. The optical density each of the unrecorded portion and the recorded image was measured with a Macbeth densitometer to evaluate the hot water resistance.

Plasticizer resistance

A wrap film (trade name: Hiwrap KMA-W, made by Mitsui Chemical) was wound 3-fold around a polypropylene pipe (40 mm diameter). A heat-sensitive recording material having formed images thereon was superposed on the film with the images directed outward and thereon was further wound a wrap film three-fold. After standing at 40°C for 24 hours, the optical density of the images was measured with the above Macbeth densitometer, whereby the recording material was assessed for plasticizer resistance.

Evaluations of recording properties described above were

conducted in the same manner as those in the present specification.

Table 1

	Pigment in heat-sesitive layer		Recording density		Heat resistance	Light resistance		Water resistance	Hot water resistance		Plasticizer resistance
	Pigment	Content	Unrecorded portion	Recorded portion	Unrecorded portion	Unrecorded portion	Recorded portion	Recorded portion	Unrecorded portion	Recorded portion	Recorded portion
Experiment 1 * (= Example 1)	$Al(OH)_3$	17. 6%	0. 06	1. 37	0. 07	0. 12	1. 34	1. 32	0. 09	1. 28	1. 31
Experiment 2	$Al(OH)_3$	5. 2%	0. 06	1. 39	0. 08	0. 12	1. 35	1. 34	0. 10	1. 29	1. 32
Experiment 3	$Al(OH)_3$	44. 2%	0. 06	1. 31	0. 07	0. 11	1. 28	1. 25	0. 09	1. 22	1. 25
Experiment 4	Silica	5. 2%	0. 06	1. 35	0. 08	0. 12	1. 32	1. 34	0. 11	1. 25	1. 29
Experiment 5	Silica	44. 2%	0. 06	1. 24	0. 07	0. 12	1. 21	1. 22	0. 10	1. 20	1. 15
Experiment 6	Kaolin	5. 2%	0. 06	1. 32	0. 08	0. 12	1. 28	1. 34	0. 10	1. 26	1. 23
Experiment 7	Kaolin	44. 2%	0. 06	1. 28	0. 07	0. 11	1. 24	1. 27	0. 09	1. 22	1. 24
Experiment 8	Talc	5. 2%	0. 06	1. 34	0. 08	0. 12	1. 30	1. 31	0. 11	1. 28	1. 30
Experiment 9	Talc	44. 2%	0. 06	1. 27	0. 07	0. 11	1. 25	1. 24	0. 09	1. 22	1. 22
Comparative Experiment 1	$Al(OH)_3$	1. 8%	0. 06	1. 36	0. 12	0. 12	1. 31	1. 32	0. 21	1. 29	1. 30
Comparative Experiment 2	$Al(OH)_3$	56. 2%	0. 06	1. 18	0. 07	0. 11	1. 14	1. 15	0. 09	1. 08	1. 09
Comparative Example 1 **	$CaCO_3$	15. 5%	0. 06	1. 35	0. 07	0. 12	1. 32	1. 01	0. 34	0. 92	1. 31

* Conducted in the same manner as in Example 1 of the present specification

** Taken from Table 1 of the present specification

IV. CONCLUSION

As shown in Table 1 in the declaration, the heat-sensitive recording materials containing specific inorganic pigments used in an amount of 3 to 50 wt% based on the heat-sensitive recording layer (Experiments 1-9) exhibit excellent recording properties as compared with Comparative Experiments 1 and 2, and Comparative Example 1.

* * *

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: January 15, 2004

Nobuyuki Iwasaki

Nobuyuki IWASAKI